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Electronic Supplementary Information

Synthesis, structure and optical property of tetraphenylethene derivatives with through-space conjugation between benzene and various planar chromophores

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1. General

Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under dry nitrogen immediately prior to use. All chemicals and reagents were purchased from commercial sources and used as received without further purification. ^{1}H and ^{13}C NMR spectra were measured on a Bruker AV 500 spectrometer or Bruker AV 300 spectrometer in appropriate deuterated solution at room temperature. High resolution mass spectra (HRMS) were recorded on a GCT premier CAB048 mass spectrometer operating in MALDI-TOF mode. Single crystal X-ray diffraction intensity data were collected on a Bruker–Nonices Smart Apex CCD diffractometer with graphite monochromated MoKα or CuKa radiation. Processing of the intensity data was carried out using the SAINT and SADABS routines, and the structure and refinement were conducted using the SHELTL suite of

X-ray programs (version 6.10). UV-vis absorption spectra were measured on a Shimadzu UV-2600 spectrophotometer. Photoluminescence spectra were recorded on a Horiba Fluoromax-4 spectrofluorometer. Fluorescence quantum yields were measured using a Hamamatsu absolute PL quantum yield spectrometer C11347 Quantaurus-QY. The ground-state and excited state geometries were optimized using the density function theory (DFT) method with ωB97XD hybrid functional at the basis set level of 6-31g*. All the calculations were performed using Gaussian 09 package.

2. Synthesis and Characterization

General procedures for the synthesis of *o*-TPEAr: A mixture of compound *o*-TPEBr[1] (5 mmol), arylboronic acid (6 mmol), $Pd(PPh_3)_4$ (0.58 g, 0.5 mmol), and potassium carbonate (3.5 g, 25 mmol) in 100 mL of toluene/ethanol/water (8/1/1 v/v/v) was heated to reflux for 12 h under nitrogen. The reaction mixture was cooled to room temperature, poured into water, and extracted twice with dichloromethane. The combined organic layers were washed with saturated brine solution and water, and dried over anhydrous magnesium sulfate. After filtration and solvent evaporation, the residue was purified by silica-gel column chromatography using hexane/dichloromethane as eluent.

***o*-TPEPh:** White solid, yield 85%. ^{1}H NMR (500 MHz, $CDCl_3$), δ (TMS, ppm): 7.25–7.11 (m, 7H), 7.09–7.05 (m, 5H), 7.02–6.96 (m, 6H), 6.95–6.93 (m, 2H), 6.90–6.87 (m, 2H), 6.49–6.46 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$), δ (TMS, ppm): 143.9, 143.8, 143.0, 142.0, 141.9, 141.4, 141.1, 138.6, 132.8, 131.4, 131.2, 130.9, 130.3, 128.8, 127.6, 127.5, 127.3, 127.2, 127.1, 126.8, 126.3, 126.2, 126.1, 126.0. HRMS ($C_{32}H_{24}$): *m/z* 408.1868 (M + Na^+, calcd 431.1878).

***o*-2-TPENp:** White solid, yield 80%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (TMS, ppm): 7.75–7.59 (m, 3H), 7.47–7.36 (m, 3H), 7.29–7.22 (m, 5H), 7.11–6.90 (m, 11H), 6.78–6.73 (m, 2H), 6.29 (d, 2H, J = 7.8 Hz). ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 144.6, 144.5, 142.7, 142.2, 139.8, 139.1, 134.1, 133.6, 132.7, 132.2, 131.9, 131.5, 131.2, 128.8, 128.5, 128.2, 128.1, 128.0, 127.7, 127.6, 127.2, 127.0, 126.9, 126.7, 126.2, 126.1. HRMS ($C_{36}H_{26}$): *m/z* 458.2032 (M^+, calcd 458.2035).

***o*-TPEAn:** White solid, yield 75%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (TMS, ppm): 8.21 (s, 1H), 7.82 (br, 2H), 7.47 (dd, J = 8.2, 1.1 Hz, 2H), 7.38–7.15 (m, 12H), 6.98–6.89 (m, 1H), 6.84–6.79

(m, 3H), 6.58–6.55 (m, 2H), 6.25–6.13 (m, 3H), 5.90–5.87 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 144.4, 144.1, 143.4, 142.5, 141.9, 141.2, 139.7, 137.3, 134.4, 133.8, 131.7, 131.3, 131.0, 130.7, 130.2, 128.6, 128.4, 127.7, 127.5, 127.2, 127.0, 126.9, 126.3, 126.2, 125.2, 125.0, 124.9. HRMS ($C_{40}H_{28}$): *m*/*z* 508.2151 (M^+, calcd 508.2191).

***o*-TPEPa:** White solid, yield 72%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (TMS, ppm): 8.64–8.45 (m, 2H), 7.84–7.07 (m, 17H), 6.91–6.77 (m, 5H), 6.62–6.56 (m, 1H), 6.36–6.27 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 144.1, 141.5, 140.7, 134.5, 133.5, 133.1, 132.6, 132.2, 131.9, 131.6, 131.3, 129.5, 129.3, 128.4, 128.1, 127.8, 127.7, 127.6, 127.2, 127.0, 126.9, 126.3, 126.2, 126.1, 126.0, 125.4, 123.0, 122.8, 122.6. HRMS ($C_{40}H_{28}$): *m*/*z* 508.2191 (M^+, calcd 508.2191).

***o*-TPEPy:** White solid, yield 68%. The products of *o*-TPEPy are isomeric mixtures, and thus the peaks are hard to be integrated. The major isomeric product is discussed in the paper. ^{1}H NMR (300 MHz, $CDCl_3$) δ (TMS, ppm): 8.19–8.16 (m), 8.13–8.16 (m), 8.01–7.90 (m), 7.62–7.58 (m), 7.42–7.32 (m), 7.28–7.12 (m), 6.95–6.93 (m), 6.89–6.87 (m), 6.78–6.77 (m), 6.71–6.68 (m), 6.35–6.32 (m), 6.21–6.19 (m), 6.09–6.07 (m), 6.03–5.99 (m), 5.84–5.81 (m). ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 145.3, 144.8, 144.0, 142.9, 142.5, 141.1, 138.6, 137.9, 137.4, 134.6, 133.7, 132.5, 131.9, 131.7, 131.5, 131.4, 130.8, 130.6, 130.1, 128.3, 128.1, 127.9, 127.7, 127.4, 127.3, 127.1, 126.8, 126.3, 125.2, 125.0, 124.5, 124.0. HRMS ($C_{42}H_{28}$): *m*/*z* 532.2198 (M^+, cald 532.2191).

X-ray crystallography

Crystal data for *o*-TPEPh (CCDC 1432503): $C_{32}H_{24}$, MW = 408.51, monoclinic, P2(1)/n, a = 9.4248(7), b = 9.6366(7), c = 25.0543(16) Å, β = 94.474(2)°, V = 2268.6(3) Å^3, Z = 4, Dc = 1.196 g cm^{-3}, μ = 0.068 mm^{-1} (MoKα, λ = 0.71073), F(000) = 864, T = 173(2) K, $2\theta_{max}$ = 25.360 (97.1%)°, 12809 measured reflections, 4044 independent reflections (R_{int} = 0.0495), GOF on F^2 = 1.043, R_1 = 0.0816, wR_2 = 0.1000 (all data), Δe 0.141 and –0.166 eÅ^{-3}.

Crystal data for *o*-2-TPENp (CCDC 955717): $C_{36}H_{26}$, MW = 458.57, triclinic, P-1, a = 9.2253(12), b = 12.0172(19), c = 12.8207(16) Å, α = 65.023(14)°, β = 76.245(11)°, γ = 83.655(12)°, V = 1251.4(3) Å^3, Z = 2, Dc = 1.217 g cm^{-3}, μ = 0.520 mm^{-1} (CuKα, λ = 1.5418), F(000) = 484, T = 143 K, $2\theta_{max}$ = 66.5 (97.4%)°, 7446 measured reflections, 4372 independent reflections (R_{int} = 0.0420), GOF on F^2 = 1.003, R_1 = 0.0532, wR_2 = 0.0973 (all data), Δe 0.169

and –0.210 eÅ^{-3}.

Crystal data for *o*-TPEAn (CCDC 1432504): $C_{40}H_{28}$, *MW* = 508.62, monoclinic, P21/c, *a* = 16.4844(14), *b* = 9.1722(12), *c* = 19.225(3) Å, β = 107.472(12)°, *V* = 2772.7(6) Å^3, *Z* = 4, *D*c = 1.218 g cm^{-3}, μ = 0.521 mm^{-1} (CuKα, λ = 1.54178), *F*(000) = 1072, *T* = 143 K, $2\theta_{max}$ = 66.5 (97.3%)^o, 9173 measured reflections, 4859 independent reflections (R_{int} = 0.0395), GOF on F^2 = 1.006, R_1 = 0.0563, wR_2 = 0.0872 (all data), Δe 0.149 and –0.207 eÅ^{-3}.

Crystal data for *o*-TPEPa (CCDC 1432505): $C_{40}H_{28}$, *MW* = 508.62, monoclinic, P2(1)/n, *a* = 11.3717(2), *b* = 15.9519(3), *c* = 15.1309(3) Å, β = 93.429(2)°, *V* = 2739.83(9) Å^3, *Z* = 4, *D*c = 1.233 g cm^{-3}, μ = 0.528 mm^{-1} (CuKα, λ = 1.54178), *F*(000) = 1072, *T* = 173(2) K, $2\theta_{max}$ = 66.5 (97.7%)^o, 9542 measured reflections, 4830 independent reflections (R_{int} = 0.0270), GOF on F^2 = 1.023, R_1 = 0.0443, wR_2 = 0.0995 (all data), Δe 0.176 and –0.172 eÅ^{-3}.

Crystal data for *o*-TPEPy (CCDC 1432506): $C_{42}H_{28}$, *MW* = 532.64, monoclinic, P121/c1, *a* = 9.5798(2), *b* = 10.2198(3), *c* = 29.4004(8) Å, β = 96.324(2)°, *V* = 2860.89(13) Å^3, *Z* = 4, *D*c = 1.237 g cm^{-3}, μ = 0.530 mm^{-1} (CuKα, λ = 1.54178), *F*(000) = 1120, *T* = 173(2) K, $2\theta_{max}$ = 66.5 (97.6%)^o, 9691 measured reflections, 5039 independent reflections (R_{int} = 0.0412), GOF on F^2 = 1.005, R_1 = 0.0723, wR_2 = 0.1135 (all data), Δe 0.305 and –0.170 eÅ^{-3}.

3. Additional data

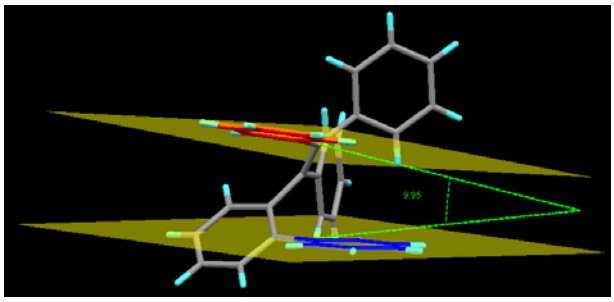

Fig. S1 Tilted angle of two cofacial stacked arenes in *o*-TPEPh.

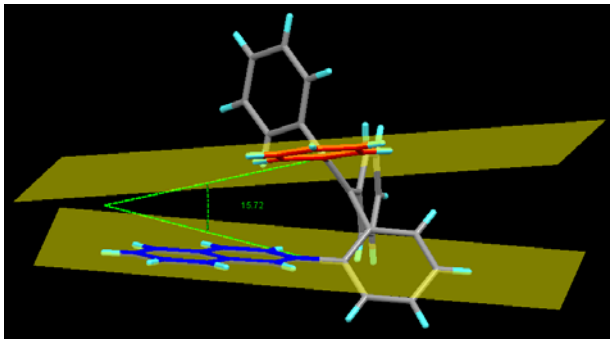

Fig. S2 Tilted angle of two cofacial stacked arenes in *o*-2-TPENp.

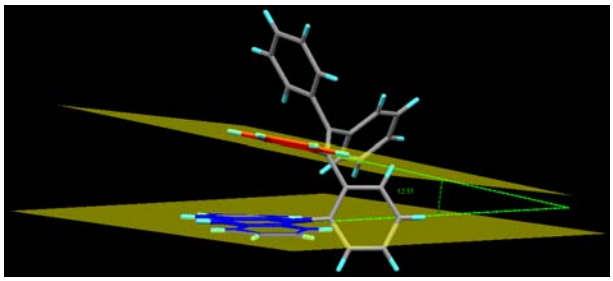

Fig. S3 Tilted angle of two cofacial stacked arenes in *o*-TPEAn.

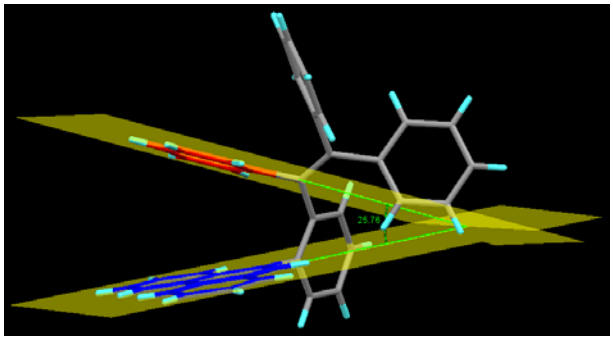

Fig. S4 Tilted angle of two cofacial stacked arenes in *o*-TPEPa.

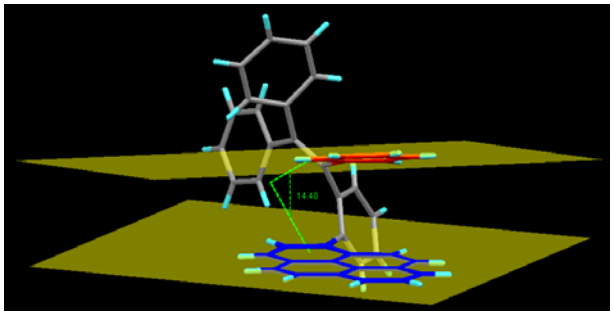

Fig. S5 Tilted angle of two cofacial stacked arenes in *o*-TPEPy.

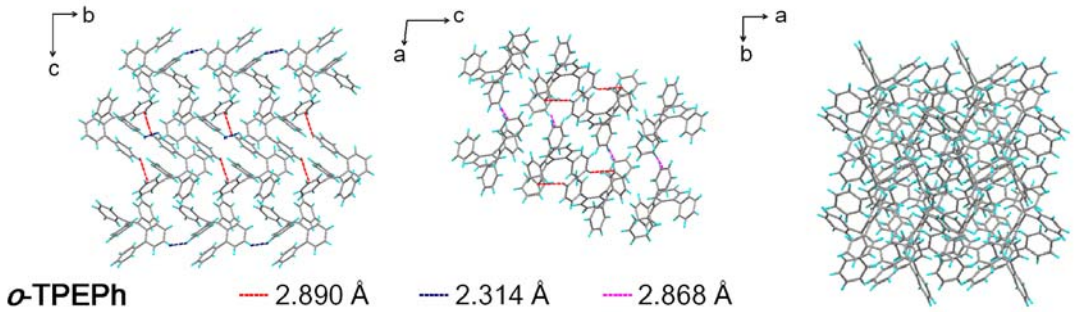

Fig. S6 Molecular packing patterns of *o*-TPEPh in the crystalline state with indicated CH–π interactions between adjacent molecules.

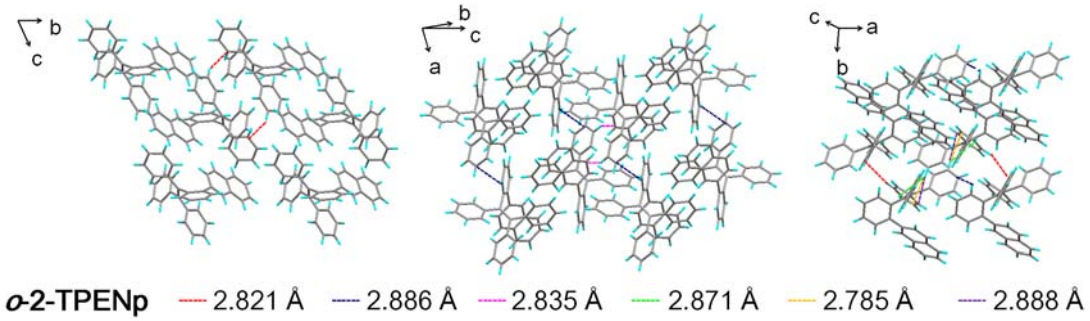

Fig. S7 Molecular packing patterns of *o*-2-TPENp in the crystalline state with indicated CH–π interactions between adjacent molecules.

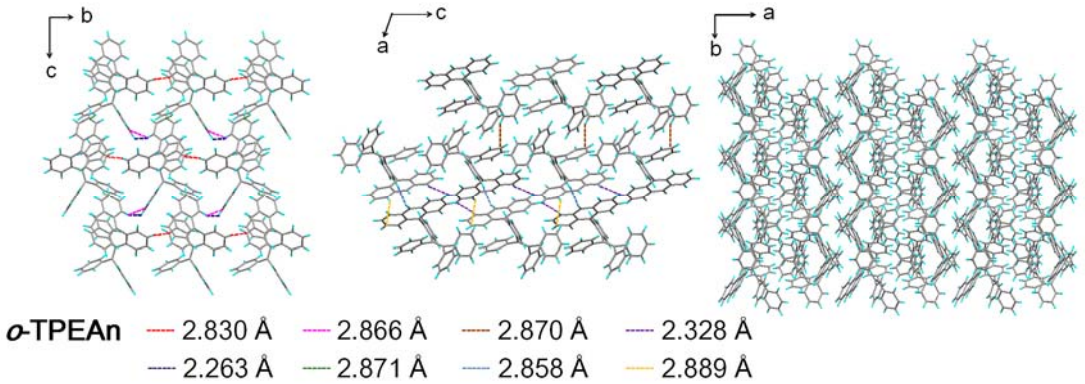

Fig. S8 Molecular packing patterns of *o*-TPEAn in the crystalline state with indicated CH–π interactions between adjacent molecules.

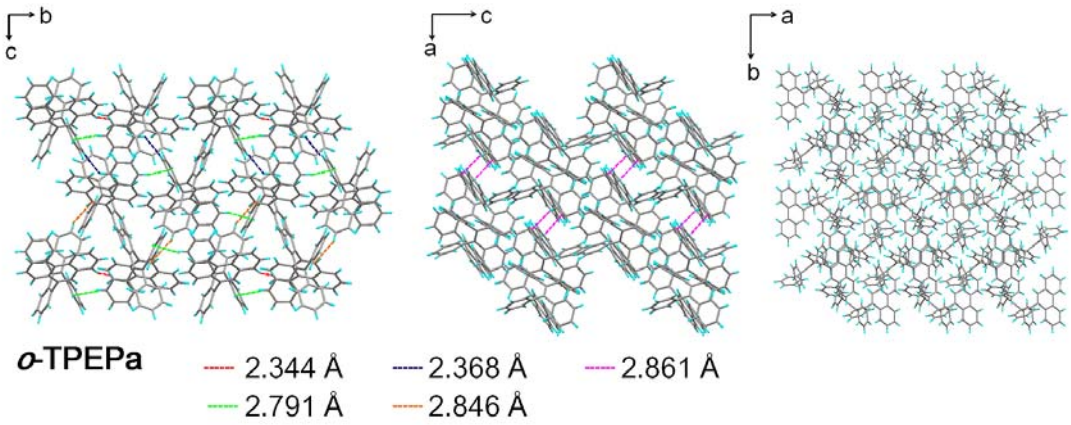

Fig. S9 Molecular packing patterns of *o*-TPEPa in the crystalline state with indicated CH–π interactions between adjacent molecules.

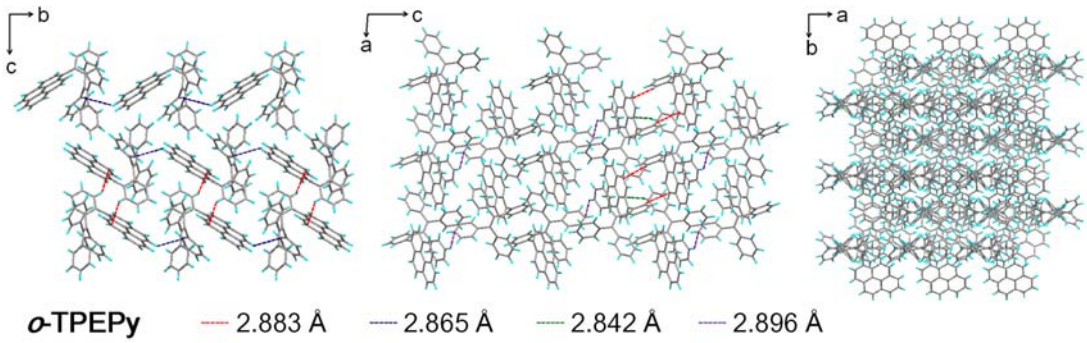

Fig. S10 Molecular packing patterns of *o*-TPEPy in the crystalline state with indicated CH–π interactions between adjacent molecules.

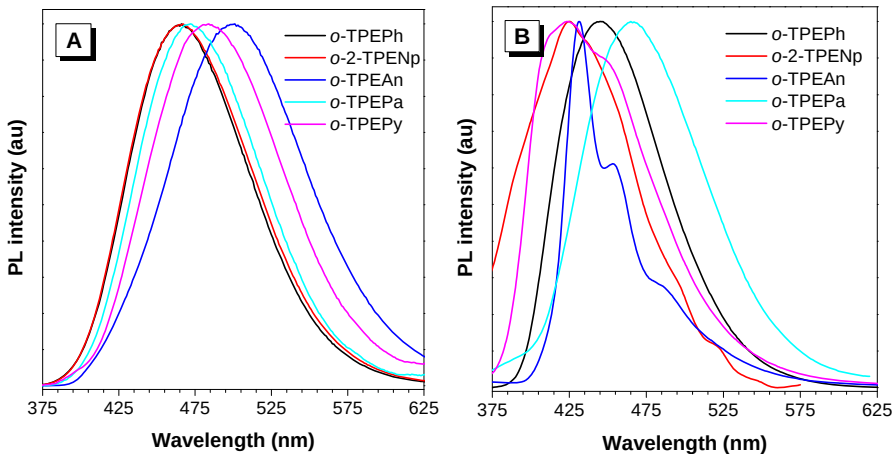

Fig. S11 Photoluminescence (PL) spectra of *o*-TPEAr in (A) films, and (B) crystals, λ_{ex} = 330 nm.

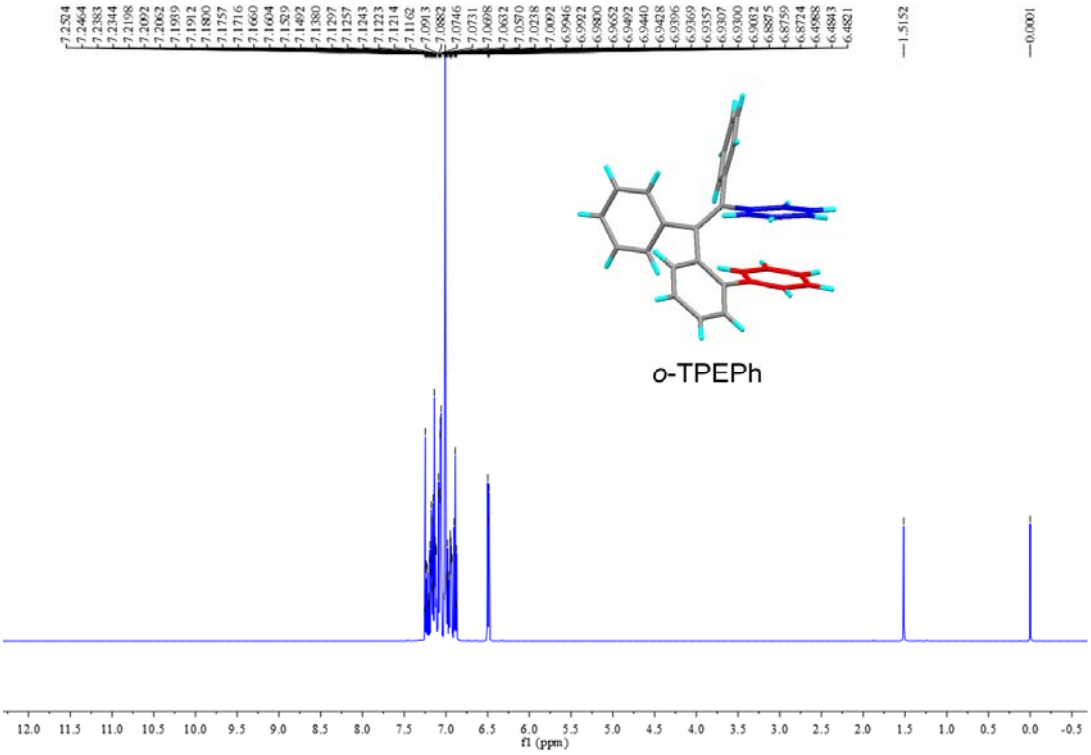

Fig. S12 ^{1}H NMR of *o*-TPEPh (500 MHz, $CDCl_3$).

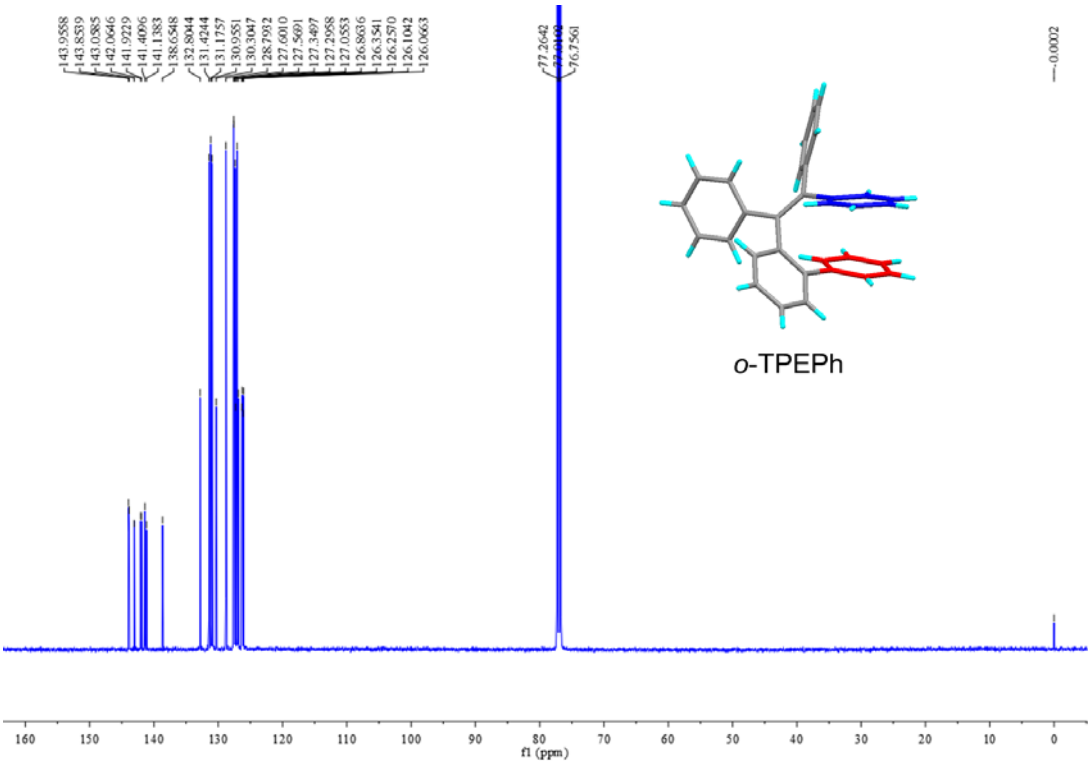

Fig. S13 ^{13}C NMR of *o*-TPEPh (125 MHz, $CDCl_3$).

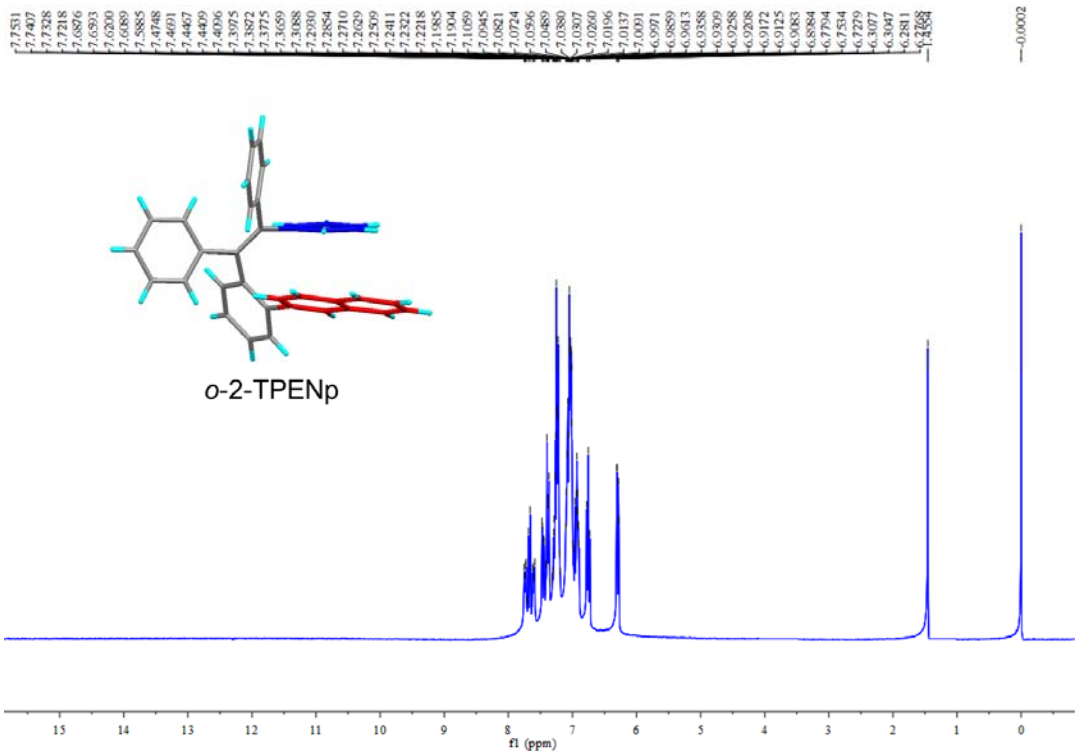

Fig. S14 ^{1}H NMR of *o*-2-TPENp (300 MHz, $CDCl_3$).

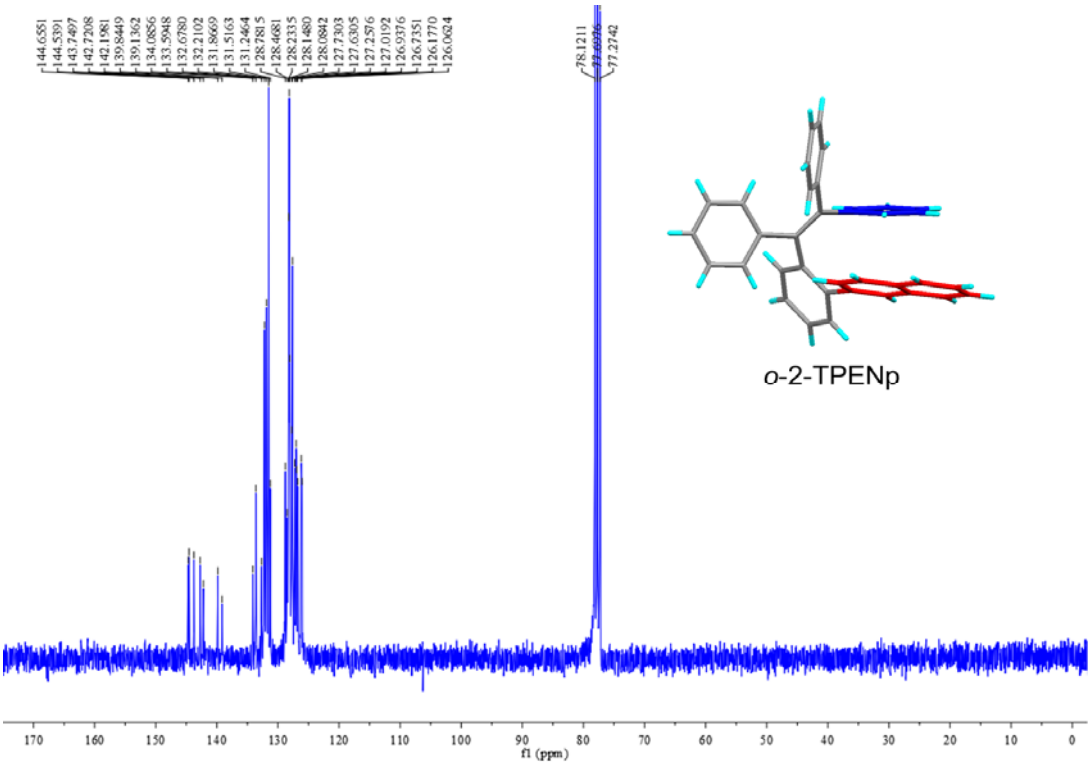

Fig. S15 ^{13}C NMR of *o*-2-TPENp (75 MHz, $CDCl_3$).

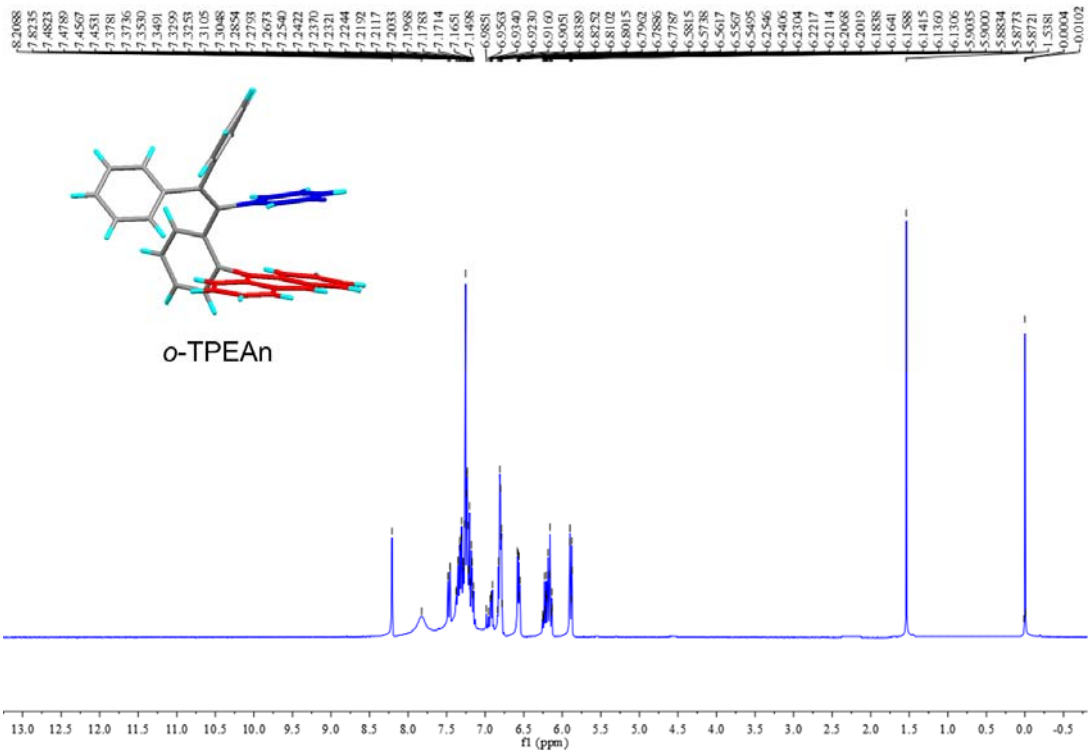

Fig. S16 ^{1}H NMR of *o*-TPEAn (300 MHz, $CDCl_3$).

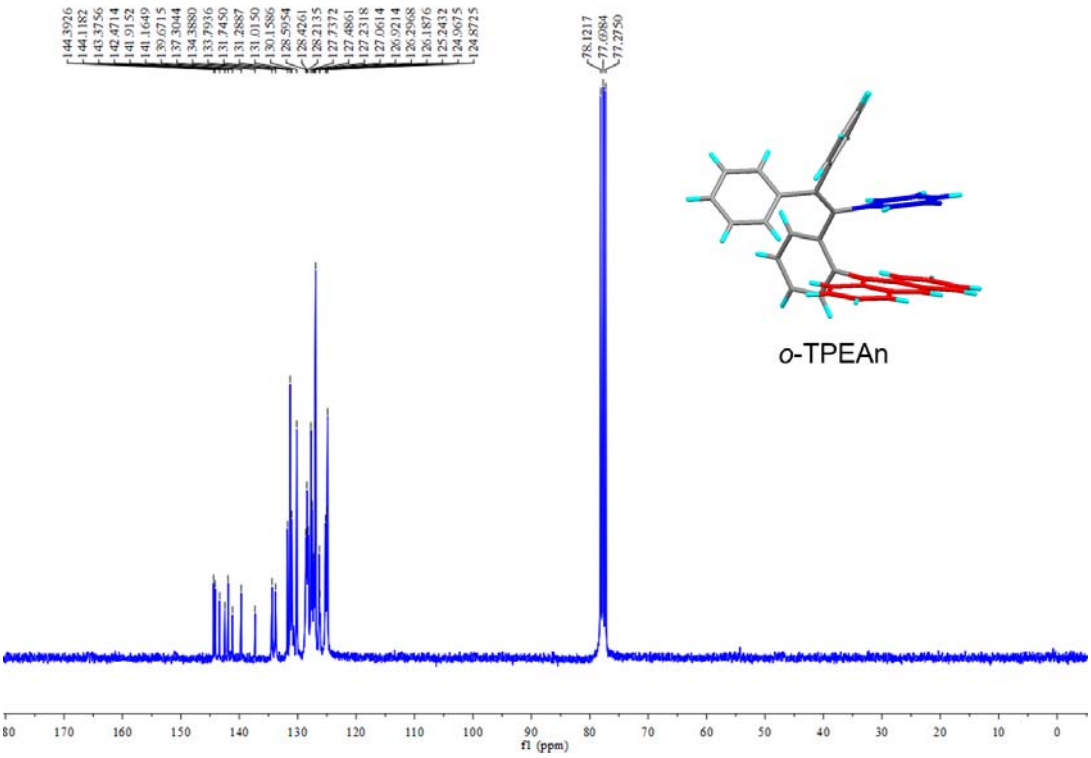

Fig. S17 ^{13}C NMR of *o*-TPEAn (75 MHz, $CDCl_3$).

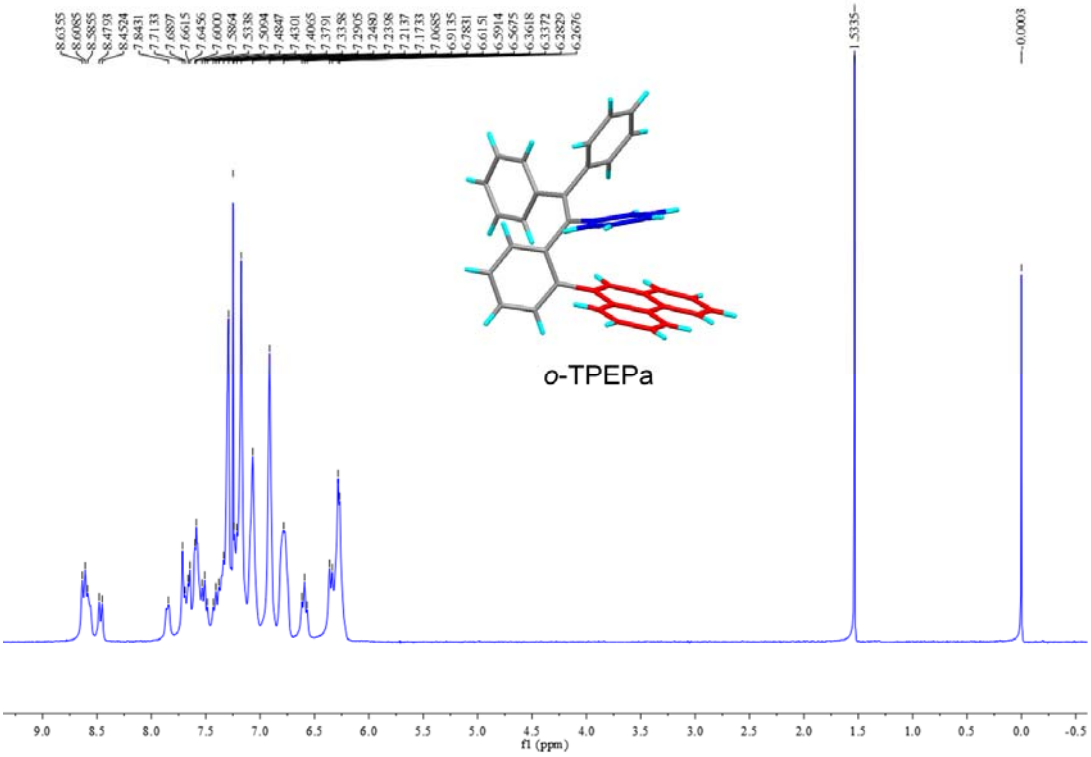

Fig. S18 ^{1}H NMR of *o*-TPEPa (300 MHz, $CDCl_3$).

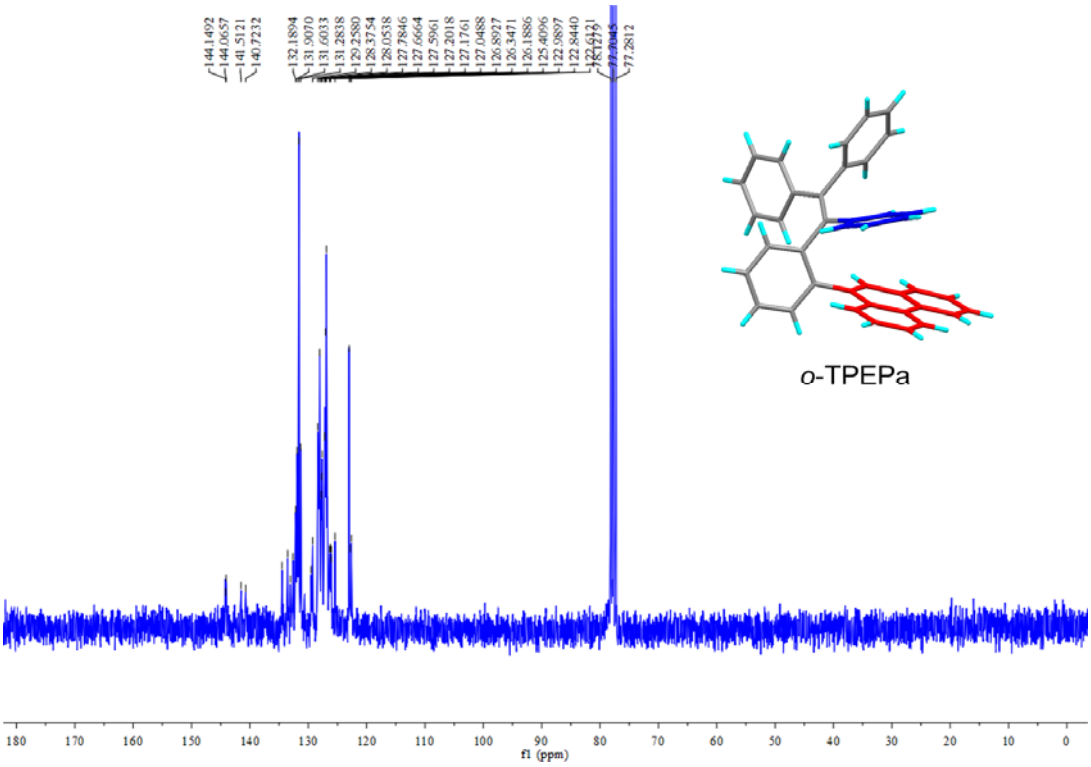

Fig. S19 ^{13}C NMR of *o*-TPEPa (75 MHz, $CDCl_3$).

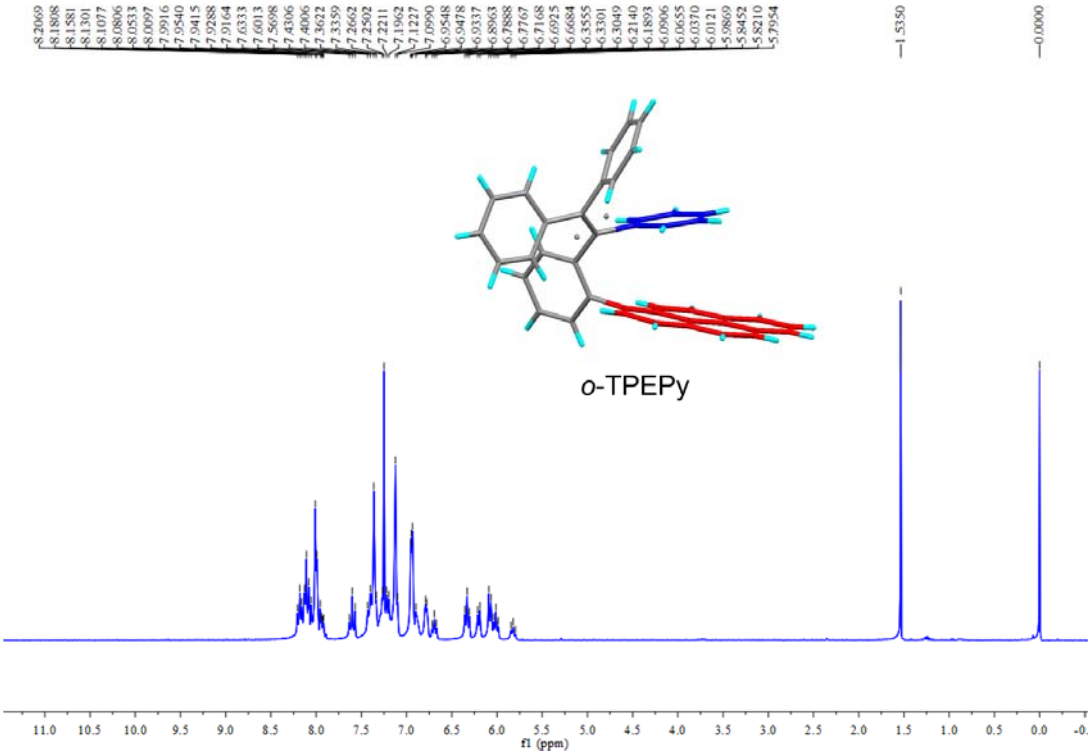

Fig. S20 ^{1}H NMR of *o*-TPEPy (300 MHz, $CDCl_3$).

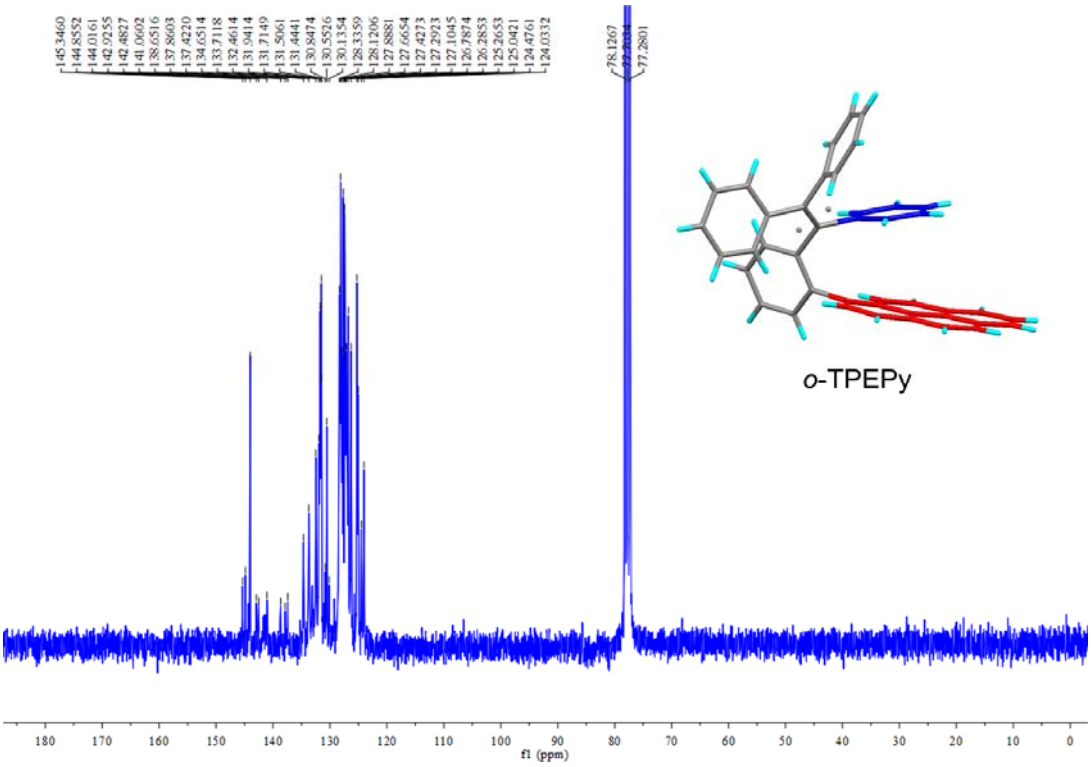

Fig. S21 ^{13}C NMR of *o*-TPEPy (75 MHz, $CDCl_3$).

4. Reference

1 J. Huang, N. Sun, Y. Dong, R. Tang, P. Lu, P. Cai, Q. Li, D. Ma, J. Qin and Z. Li, *Adv. Funct. Mater.*, 2013, **23**, 2329–2337.